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Published Version:

Stoycheva J., Tadjer A., Garavelli M., Spassova M., Nenov A., Romanova J. (2020). Boron-doped polycyclic aromatic hydrocarbons: A molecular set revealing the interplay between topology and singlet fission propensity. THE JOURNAL OF PHYSICAL CHEMISTRY LETTERS, 11(4), 1390-1396 [10.1021/acs.jpcllett.9b03406].

Availability:

This version is available at: <https://hdl.handle.net/11585/785782> since: 2020-12-28

Published:

DOI: <http://doi.org/10.1021/acs.jpcllett.9b03406>

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Joanna Stoycheva, Alia Tajer, Marco Garavelli, Milena Spassova, Artur Nenov and Julia Romanova “Boron-doped polycyclic aromatic hydrocarbons: a molecular set revealing the interplay between topology and singlet fission propensity” in Journal of Physical Chemistry Letters, 11 (2020), 1390-1396

The final published version is available online at:
<https://dx.doi.org/10.1021/acs.jpcllett.9b03406>

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Boron-Doped Polycyclic Aromatic Hydrocarbons: A Molecular Set Revealing the Interplay between Topology and Singlet Fission Propensity

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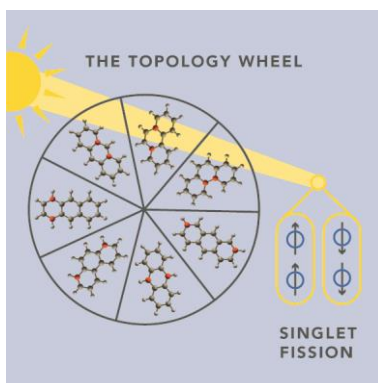
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ABSTRACT

We demonstrate the relationship between topology (the way in which the atoms are connected), open-shell character and singlet fission (SF) propensity in a series of diboron-doped anthracenes and phenanthrenes. The study is performed by using high level wavefunction based quantum-

chemical calculations. The results show that the molecular topology plays a crucial role for the optical properties and, respectively, for the SF propensity, of the studied compounds. The topology-derived correlations between structure and properties are interpreted in the light of the Kekulé hydrocarbons concept and serve as molecular design guidelines for the discovery of new SF materials. Finally, several boron-doped polycyclic aromatic hydrocarbons are proposed as SF chromophores for organic solar cells.

TOC GRAPHICS



KEYWORDS organic solar cells, open-shell character, optical properties, RASPT2

Organic solar cells possess unique advantages over the widely used silicon solar cells: they are flexible, low-cost, light weight and environment-friendly.¹ However, organic solar cells are still characterized with low power conversion efficiency. Recently, it has been demonstrated that a successful strategy to improve the efficiency of organic solar cells is the use of materials that undergo singlet fission (SF).² In the latter, irradiation with one photon creates a molecule in a first singlet excited state (S_1), which interacts with a molecule in the ground state (S_0) and the product of this reaction are two triplet excitons (T_1). Next, the two triplet excitons dissociate into

four charge carriers instead of only two in the case where a SF process is not observed. Thus, organic solar cells have the potential to overcome the maximum theoretical efficiency of a solar cell (the Shockley-Queisser limit). It has been demonstrated that the SF process is feasible in molecules that satisfy the following demanding conditions: 1) $\Delta E_{ST} = 2E(T_1) - E(S_1) \leq 0$, i.e., the excitation energy to the first excited state, $E(S_1)$, should be larger or equal to twice the excitation energy to the lowest triplet state, $E(T_1)$, and 2) $\Delta E_{TT} = 2E(T_1) - E(T_2) \leq 0$, i.e., the excitation energy to the second triplet excited state, $E(T_2)$, should be larger or equal to twice the excitation energy to the lowest triplet excitation, $E(T_1)$.³ The first condition ensures that the split of a singlet exciton into two triplet excitons is an energetically favorable process, while the second one guarantees that the triplet-triplet annihilation will not compete with the SF. Recently, Nakano *et al.* showed that molecules with low to intermediate multiple diradical character (DRC) are good candidates for efficient SF chromophores.^{4,5,6} This requirement is related to the first feasibility condition and implies that ΔE_{ST} should be indeed ≈ 0 or slightly lower. This is important to be noted because molecules with too high DRC may satisfy the $\Delta E_{ST} = 2E(T_1) - E(S_1) \leq 0$ condition but in that case $E(T_1)$ is very small and the energy loss in the SF process $|2E(T_1) - E(S_1)|$ is large. Systems with a significant DRC often possess a “dark” S_1 state which is well separated from the first dipole-allowed singlet excited state. As SF requires two partners, the reaction is diffusion-limited. At the same time internal relaxation processes in polycyclic aromatic hydrocarbons (PAHs) occur on a few-hundred femtosecond timescale.⁷ Thus, following an excitation to a dipole-allowed excited state, a fast internal conversion to the “dark” S_1 state is expected, whose long-lived nature will be favorable for the quantum efficiency. The diffusion limit can be surpassed by linking partners through covalent bonds⁸, in which case SF from higher lying electronic states is expected to compete with internal conversion. The role of a “dark” S_1

state in the SF process is still not clear.⁹ Therefore, in this work we have evaluated the SF compliance with respect to the lowest electronic state, thus assuring that the $\Delta E_{ST} \leq 0$ condition is automatically fulfilled for any higher-lying state.

Typical examples of efficient SF chromophores are acenes, oligophenyls, polyenes, carotenoids and diradicaloids.^{2,3,10,11} New acenes-based SF compounds were recently designed by 1) variation in the conjugation length and 2) doping with heteroatoms (N-, Si-, as well as B- and N-simultaneously).^{10,12-15} Here, we propose B-doping of PAHs, so far underexplored in SF aspect, as a new strategy for the design of SF chromophores. The molecular set contains all symmetric diboron derivatives of anthracene and phenanthrene, which remain planar after geometry optimization (see **Figure 1**).¹⁶

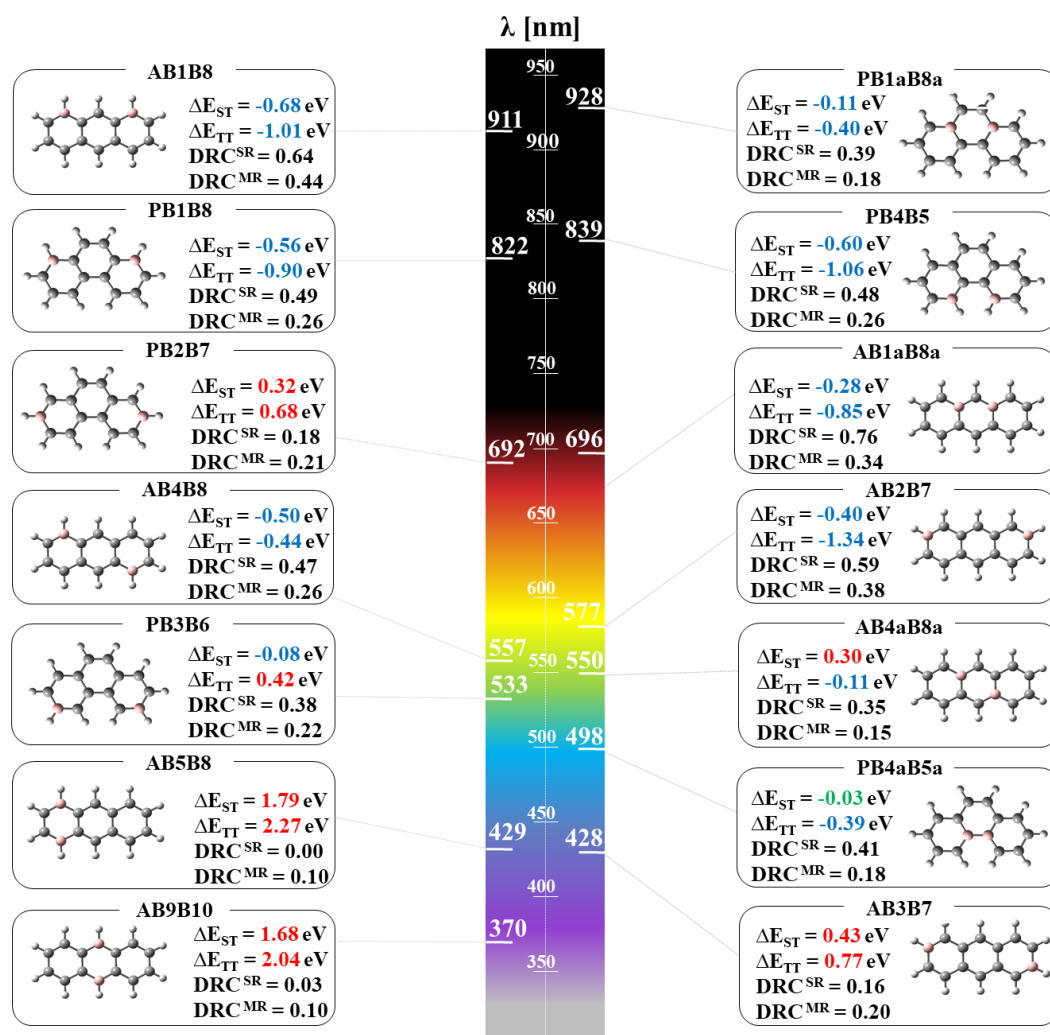


Figure 1. Molecular set investigated in this work. The compounds names contain the following labels - A (anthracene derivative), P (phenanthrene derivative), B (boron), and numbers, which show the position of the heteroatoms in accordance with the IUPAC numbering of the pristine hydrocarbons (**Figure S1**, SI). Wavelength λ [nm] of the first allowed electronic transition ($f \geq 0.02$), diradical character (DRC), ΔE_{ST} [eV] = $2E(T_1) - E(S_1)$ and ΔE_{TT} [eV] = $2E(T_1) - E(T_2)$. The DRC is estimated by using natural orbitals occupational numbers from multi-reference (DRC^{MR}) and single-reference (DRC^{SR}) calculations.

The present molecular set allows us to reveal the effect of topology (connectivity) on the SF propensity of the chromophores. The relationship between topology, open-shell character and SF propensity is established based on electronic structure calculations at the multiconfiguration wavefunction level of theory on top of MP2^{17,18} optimized ground state geometries. In particular, we rely on the RASSCF//RASPT2 protocol, which involves restricted active space self-consistent field calculations¹⁹ followed by multi-reference second order perturbation theory^{20,21} (**SI, Computational Methods**). The use of multi-reference second order approach allows us to take into account both static and dynamic electron correlation effects, which are necessary for the accurate description of open-shell molecules.²² Moreover, in molecules with a pronounced diradical character, the doubly excited states contribute sizeable to the low energy electronic spectrum. Compared to single-reference methods (such as TD-DFT), this protocol allows to describe doubly excited states at equal footing with single excitations, which is essential for assessing the SF propensity. The diradical character is estimated by using natural orbital occupational numbers from single state (SS)-RASSCF/aug-cc-pVDZ (DRC^{MR}) and UNO/6-31G**²³ (DRC^{SR}) calculations (See **SI, Computational protocol**). Geometry optimization was performed with Gaussian 09²⁴, while electronic structure calculations were executed with the MOLCAS 8²⁵ suite. The results for the newly proposed chromophores are interpreted in terms of stability and the Kekulé structure concept.

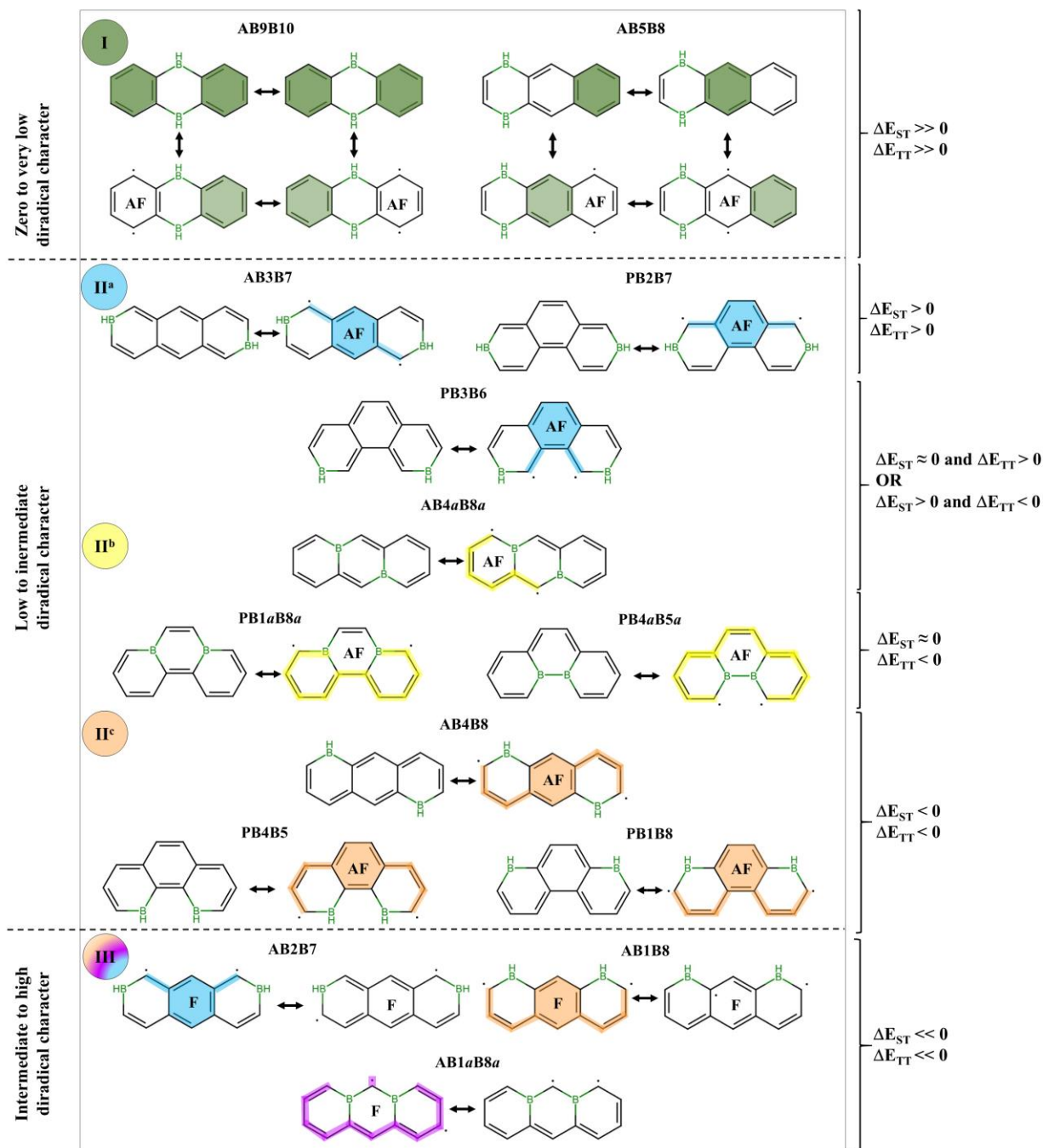


Figure 2. Classification of the diboron-doped anthracenes and phenanthrenes in three groups based on the relationship between structure, diradical character and SF propensity. Selected resonance structures and type of spin-spin exchange: AF=antiferromagnetic and F=ferromagnetic.

The SF process was observed for the first time in the crystalline form of one of the parent compounds investigated here - anthracene (**A**) by laser generation.²⁶ The other parent compound - phenanthrene (**P**), however, has not been investigated for SF proclivity.³ The electronic spectra of the parent compounds (**SI, Table S1-S2**) are characterized with a bright state (375 nm and $f=0.09$ for **A**, 300 nm and $f=0.07$ for **P**, leading configuration $H \rightarrow L$) and a dark state (leading configurations $H-1 \rightarrow L$ & $H \rightarrow L+1$) above 300 nm. While the absorption wavelength and oscillator strength of the bright state of **A** and **P** allow conversion of sunlight, the triplet energetics do not satisfy the SF feasibility conditions (**SI, Table S3**). The reason lies in the stability of the aromatic system, which obeys the $4n+2$ Hückel rule and gives rise to a singlet ground state (denoted S_0) with a zero to very low DRC. A common practice for increasing the DRC character and SF-propensity of acenes concerns doping with heteroatoms of higher (nitrogen) and/or lower (boron) valence. Diboron-doping will reduce the π -electrons with 2, which will transform the parent compounds into $4n$ antiaromatic systems and is expected to increase their diradical character.^{27,28}

Figure 1 summarizes the key results obtained for 14 diboron-doped anthracenes and phenanthrenes. It demonstrates the crucial impact of the molecular topology on the absorption properties of the boron-doped compounds. The wavelength of the first allowed singlet transition varies from the near-UV (370 nm, **PB5B8**) to the near-IR (928 nm, **PB1aB8a**) region. Consistent with previous theoretical predictions, we observe that: a) the oscillator strength of the first excited state (denoted S_1) decreases with the increase of the diradical character²⁹ and S_1 is essentially dark in the majority of compounds; b) the doubly excited configuration $H,H \rightarrow L,L$ acquires a dominant role in the wavefunctions of the lowest electronic states³⁰ (**SI, Tables S3 and S5**). Based on the topology–SF propensity relationship, we group the studied compounds in

three groups as shown in **Figure 2**. Doping anthracene at opposite C-centers of the same ring (**AB9B10**, **AB5B8**, group **I**) *does not* satisfy the SF feasibility conditions, as both parameters ΔE_{ST} and ΔE_{TT} result highly endoergic. The compounds from group **I** are similar to parent anthracene. They are characterized with a ground state S_0 with zero to low DRC and a bright S_1 state absorbing in the near-UV. The stability of their closed-shell configuration can be understood in the light of the Clar's aromatic sextet theory.³¹ In the case of **AB9B10** one can write down Kekulé formulas with two isolated Clar's sextets in the ground state structure representation, whereas **AB5B8** can be represented by Kekulé formulas with one migrating Clar's sextet (**Figure 2**). An additional confirmation for the closed-shell character of the compounds from group **I** is that their non-Kekulé structures contain two unpaired electrons that interact in an antiferromagnetic way via spin polarization mechanism (**Figure 2** and **Figure S3, SI**).³² Correspondingly, **AB9B10** (and its @boron-substituted derivatives) is also the only experimentally available compound among all isomers and it was observed to polymerize through three-center two-electron B–H–B bonds.^{33,34} Such a polymerization process is hampered when an appropriate substituent is introduced to the B-center. **AB5B8** is only 10 kcal/mol less stable than **AB9B10** and has not been observed experimentally so far. However, similar diboron-doped compounds have been synthesized very recently.³⁵

The results obtained for group **I** compounds demonstrate that a more pronounced perturbation of the conjugated system is required in order to make anthracenes and phenanthrenes SF-compliant. Indeed, one could envision boron-doped topologies which favor an open-shell ground state with an intermediate-to-high diradical character ($DRC^{SR} > 0.50$, $DRC^{MR} > 0.30$), such as **AB1B8**, **AB1aB8a**, **AB2B7** (group **III**, **Figure 2**). These compounds cannot be represented by a Kekulé formula and even their ground state structures possess two unpaired electrons, which interact in a

ferromagnetic way via spin-polarization mechanism. Correspondingly, they exhibit a low-lying dark S_1 state and a first triplet state T_1 , which is nearly degenerate with the ground state (e.g. S_1 - $S_0 = 0.54$ eV and T_1 - $S_0 = 0.07$ eV for **AB2B7**). These compounds fulfill the SF conditions but the parameter ΔE_{ST} is excessively exoergic (**Figure 1** and **SI, Table S3**). The value of ΔE_{ST} ensues even more negative if one considers the energy introduced in the system by exciting to the first bright state (S_n) which absorbs in the visible range around 600 nm (~ 2.0 eV). Thus, albeit possible, SF in **AB1B8**, **AB1aB8a** and **AB2B7** is expected to occur with substantial energy losses.

The compounds from group **III** are suboptimal for SF applications due to the low energy conversion efficiency, yet they clearly demonstrate that slight structural modifications drastically alter the electronic and optical properties of PAHs.³⁶ Naturally, one could ask if diboron-doped anthracenes and phenanthrenes, which exhibit properties in-between those of groups **I** and **III**, exist. Our calculations give an affirmative answer for all molecules with low to intermediate DRC from group **II**. Thereby, as a function of their structure and SF-propensity, we distinguish between group **II^a** (**AB3B7**, **PB2B7** and **PB3B6**), group **II^b** (**AB4aB8a**, **PB1aB8a**, **PB4aB5a**), and group **II^c** (**AB4B8**, **PB1B8**, **PB4B5**).

Compounds from group **II^a** lie ~ 30 kcal/mol above **AB9B10** and for them one can formulate a closed-shell quinoid structure and a non-Kekule formula with two spin centers and one Clar's sextet (**Figure 2**). Their non-Kekulé structures contain *o*- and *p*- xylylene diradical fragments in which an antiferromagnetic spin exchange is observed. Therefore, their ground state is still singlet but with an open-shell character, confirmed by the intermediate diradical character ($0.16 < DRC^{SR} < 0.38$, $DRC^{MR} \approx 0.20$). Group **II^a** compounds show a very intense absorption band at 533 nm (**PB3B6** with *o*- xylylene fragment) and around 430 nm (**AB3B7** and **PB2B7** with *p*-

xylylene fragment) with an order of magnitude more intense oscillator strength as compared to the parent molecules. They exhibit a dark S_1 state ($H \rightarrow L$ or $H-1 \rightarrow L$) around 1.8-1.9 eV and a triplet state T_1 around 0.9-1.2 eV. One of them - **PB3B6**, fulfills at most the first SF feasibility condition, namely $\Delta E_{ST} \approx 0$. However, all compounds in the group possess low-lying second triplet state (T_2) so that the parameter ΔE_{TT} results highly exoergic.

Compounds from group **II^b** are characterized by a weak absorption band (S_n) in the visible region around 2.2-2.8 eV (450-500 nm) and a dark S_1 state ($H \rightarrow L$) around 1.2 eV. The electronic configurations of these weak absorption bands are dominated by double excitations: $H, H \rightarrow L, L$ for **AB4aB8a** and $H-1, H \rightarrow L, L$ for **PB1aB8a** and **PB4aB5a**. Their lowest triplet state T_1 is situated around 0.6 eV and is separated from T_2 by more than 0.9 eV. Thus, group **II^b** compounds fulfill the second SF feasibility condition and guarantee that ΔE_{ST} is only slightly endoergic (**PB1aB8a**, **PB4aB5a**) or exoergic (**AB4aB8a**). Indeed, these compounds show a low to intermediate diradical character ($0.39 \leq DRC^{SR} \leq 0.41$, $0.15 < DRC^{MR} < 0.18$), in agreement with Nakano's observations.⁴⁻⁶ It is important to realize that on the one hand, the low to intermediate DRC is a requirement for SF but on the other hand, open-shell molecules are usually unstable in air and highly reactive. In this context, despite exhibiting attractive photophysical properties, group **II^b** compounds do not allow formulation of Kekulé structures having Clar's sextets (**Figure 2**). Instead, they can be represented by a closed-shell and open-shell polyene structures, with antiferromagnetic exchange of the two unpaired electrons in the latter. One representative of group **II^b** is among the most unstable compounds in the series (e.g. **PB4aB5a** is ~ 50 kcal/mol above **AB9B10**).¹⁶ It has been demonstrated that the relative stability of the boron-doped acenes can be sterically improved by replacing the boron hydrogen by bulky substituents.^{Error! Bookmark not defined.} Unfortunately, this strategy cannot be applied to the group **II^b**

compounds because their boron atoms are coordinated with three carbons (BC3-coordination). However, stabilization can be expected also by introducing substituents to carbon spin centers. To our knowledge, such synthetic strategy was successfully applied to other diradicals but is so far underexplored for boron-doped polycyclic aromatic hydrocarbons.³⁷ In addition, the promising results for the feasibility conditions in group **II^b** suggest that synthetically-available boron-doped graphene and nanotubes with BC3-coordination can also be regarded as SF-materials.³⁸

Group **II^c** compounds (**AB4B8**, **PB1B8**, **PB4B5**) are characterized with intermediate DRC ($\text{DRC}^{\text{SR}} \approx 0.48$, $\text{DRC}^{\text{MR}} = 0.26$). Their structure can be represented by a Kekulé formula of quinoid type and a non-Kekulé formula with two unpaired electrons interacting antiferromagnetically. Their non-Kekulé formulas contain *o*- or *p*-divinylbenzene diradical fragments, which makes them analogues of group **II^a** compounds with longer conjugated path between the spin centers. This naturally results in a bathochromic shift of $S_0 \rightarrow S_1$ and $T_0 \rightarrow T_1$ transitions with respect to the **II^a** analogues, as well as in endoergic ΔE_{ST} and ΔE_{TT} feasibility conditions. The first bright states of the **II^c** molecules can be approximated with H \rightarrow L transitions and are located at 2.23 eV (S_2 , **AB4B8**) and around 1.5 eV (S_1 , **PB1B8** and S_1 , **PB4B8**). A drawback of the latter, however, is that their bright transition falls outside of the visible spectrum where the solar radiation has a low cross section, thus making energy conversion less effective. **PB1B8** instead exhibits another bright transition around 2.6 eV facilitating its more efficient exploitation. Based on the performed calculations, it is expected that a SF process in **II^c** compounds will occur with substantial energy losses. In respect of stability, the molecules from this group lie \sim 25-38 kcal/mol above the **AB9B10** isomer.

The present *ab initio* study demonstrates by means of state-of-the-art multiconfigurational wavefunction calculations that boron-doping of PAHs and variation of molecular topology are successful strategies for the in silico design of SF chromophores. Overall, our calculations demonstrate that boron-doping offers a viable and intriguing alternative to size expansion in PAHs for generating SF compliant molecular systems. The Kekulé concept was applied in order to reveal the interplay between molecular topology, open-shell character and SF propensity of the investigated compounds. Based on their photophysical properties, the following boron-doped compounds are proposed as new potential SF materials for application in organic solar cells – **AB4aB8a**, **PB1aB8a** and **PB4aB5a** with BC3-coordination (group **II^b**), as well as **AB4B8** and **PB1B8** (group **II^c**). **AB4aB8a**, **PB1aB8a** and **PB4aB5a** allow for nearly lossless singlet-to-triplet energy conversion ($\Delta E_{ST} \approx 0$). However, group **IIa** compounds show a relatively weak cross section around 500 nm and are very unstable. The aforementioned drawbacks can be remedied to a great extent in **AB4B8** and **PB1B8**, showing a high absorption cross section in the visible range and more pronounced stability which come at the cost of efficient solar energy conversion ($\Delta E_{ST} \approx -0.5$ eV) with high energy losses. Based on these findings we propose that fine tuning of the SF propensity and stabilization in the group **II** compounds can be achieved through hydrogen substitution at the boron and/or carbon spin centers with bulkier substituent having appropriate electronic properties. Furthermore, if we generalize the finding for the favorable presence of the BC3 motif to larger hydrocarbons, we can expect that boron-doped graphenes and carbon nanotubes can be also regarded as potential SF materials.³⁸

ASSOCIATED CONTENT

Supporting Information. Computational methods (**Discussion S1**); IUPAC numbering of anthracenes and phenanthrenes (**Figure S1**); Schematic representation of the active spaces used (**Figure S2**); Spin-spin exchange interactions (**Figure S3**); Active space benchmarking on anthracene (**Table S1**) and phenanthrene (**Table S2**); Diradical character and energetic differences - ΔE_{ST} , ΔE_{ST}^* and ΔE_{TT} (**Table S3**); Detailed electronic structure information for all compounds (**Table S3-S7**); MOs for the key electronic transitions (**Table 8-11**); Stability calculations, (**Table S12**); Tetraradical character (**Table S13**).

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The authors declare no competing financial interests.

ACKNOWLEDGMENT

The financial support of the National Research Program E+: Low Carbon Energy for the Transport and Households, DMC 577/17.08.2018, grant agreement D01-214/28.11.2018 and the SU Project 80-10-168/2019 is appreciated. Joanna Stoycheva is grateful for the Erasmus+ fellowship. Thanks are due to Maria Efremova for the graphical abstract.

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